

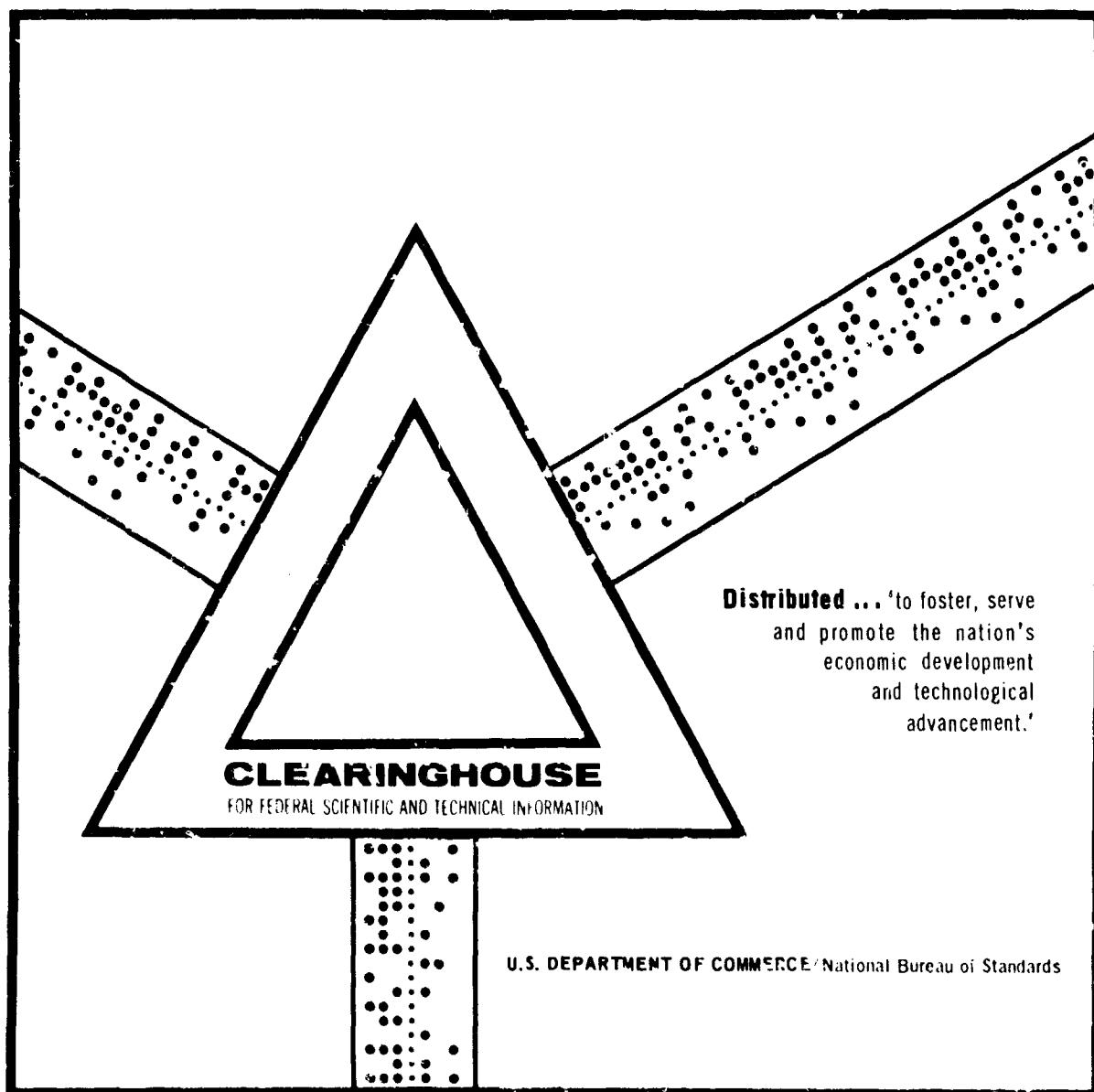
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PROCEDURES FOR THE ANALYSIS OF METALS, ALLOYS  
AND OTHER MATERIALS OF RESEARCH. PART 4--  
SPECTROPHOTOMETRIC PROCEDURES FOR THE DETER-  
MINATION OF IONS FORMED WITHIN STRESS-CORROSION  
CRACKS

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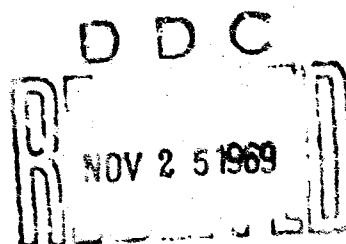
## Procedures for the Analysis of Metals, Alloys, and Other Materials of Research

### Part 4 - Spectrophotometric Procedures for the Determination of Ions Formed Within Stress-Corrosion Cracks

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October 7, 1969



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"Part 2 - Determination of Silver and Indium in Magnesium-Base Alloys, Lead in Indium, and Zirconium in Hafnium." O. R. Gates and E. J. Brooks, NRL Report 6427, Sept. 1966

"Part 3 - A Spectrophotometric Procedure for the Determination of Trace Amounts of Cobalt in Ferrous Alloys." O. R. Gates, NRL Report 6857, Dec. 1968

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## ABSTRACT

Working at final volume levels as low as 3 ml, spectrophotometric procedures have been developed for the determination of very small amounts of ferrous, ferric, and alloying-constituent ions formed within stress-corrosion cracks in carbon steels and in steels containing nickel, chromium, molybdenum, and manganese, respectively.

## PROBLEM STATUS

This is the fourth in a series of progress reports; work on the problem is continuing.

## AUTHORIZATION

NRL Problem M01-20  
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## PROCEDURES FOR THE ANALYSIS OF METALS, ALLOYS, AND OTHER MATERIALS OF RESEARCH

### Part 4—Spectrophotometric Procedures for the Determination of Ions Formed Within Stress-Corrosion Cracks

#### INTRODUCTION

This is the fourth in a series of reports concerning progress in the development of chemical methods by the Analytical Chemistry Branch, Metallurgy Division.

Qualitative chemical tests, applied directly on stress-corrosion crack surfaces of freshly broken specimens of iron-base alloys, revealed the presence of ferrous ions. To obtain a better understanding of this phenomenon, an effort has been made to determine the extent of the dissolution of iron and also of some alloying constituents.

Approximating the salt content of sea water, a 3.5% sodium chloride solution (1,2) was the medium in which the stress-corrosion tests were conducted.

To determine the extent of metallic dissolution within cracks in steel stress-corrosion specimens, spectrophotometric procedures have been applied to determine iron, nickel, chromium, molybdenum, and manganese in the microgram range. In determining each of these elements, it is generally necessary to work at a volume level that is just sufficient to be compatible with the instrumentation being used to evaluate the small amounts of iron and still smaller amounts of alloying constituents.\*

After the iron content is established spectrophotometrically, the solutions from both fracture. Surfaces of a given specimen are combined and reworked to determine the alloying elements. To avoid extensive contamination and salt pickup, only one alloying constituent is determined on a given fracture specimen. For molybdenum and manganese steels it was necessary to combine solutions from several specimens to obtain measurable amounts of the desired element.

In the carbon-steel specimens, only the iron ions were determined; in the alloyed steel specimens, iron ions and one alloying-constituent ion were determined.

#### ANALYSIS OF IRON

##### Scope

In the steel specimens tested, the amount of iron ions that formed in the stress-corrosion cracks varied between 12 and 40 micrograms, depending partially on the size of the stress-corrosion crack surfaces that developed in the different samples.

\*The minimum volume measurable with the Bausch and Lomb Spectronic 20, using the 0.5-inch-diameter absorption tubes, is about 3 ml.

### Apparatus

A spectrophotometer capable of providing transmittance data on as little as 3 ml of solution was used.

### Reagents

Ammonium Acetate Solution — Ammonium acetate (50 g) is dissolved in 400 ml of water containing 35 ml of hydrochloric acid, then diluted to 500 ml with water.

Hydroxylamine Hydrochloride Solution — Hydroxylamine hydrochloride (4 g) is dissolved in 500 ml of water.

Hydroxylamine-Ammonium Acetate Buffer Solution (pH = 4.2) — This solution is prepared fresh as required by mixing equal volumes of the ammonium acetate and hydroxylamine hydrochloride solutions.

1,10-Phenanthroline Solution — 1,10-phenanthroline (0.75 g) is dissolved in 50 ml of water at 90°C and diluted to 500 ml with water at room temperature.

Standard Iron Solution (1 ml = 10  $\mu$ g Fe) — High-purity iron (10.0 mg) is dissolved in 2 ml of water and 1 ml of nitric acid. After rinsing the cover and inner wall of the beaker with water, the solution is boiled gently to expel the oxides of nitrogen. It is then cooled and diluted to the mark in a 1000-ml volumetric flask and mixed.

### Procedure

The specimen containing the stress-corrosion crack is withdrawn from the liquid nitrogen bath and broken in a vise. The two pieces, fracture facing up, are allowed to defrost. Holding each piece so its fracture surface makes an angle of about 100 degrees with the horizontal, the fracture surface is rinsed by the dropwise addition of 1.8 ml of water from a dropping pipette. The rinsings are collected in a 3-ml test tube which is calibrated with a 2-ml mark. After adjusting the volume to the 2-ml mark, the solution is thoroughly mixed. A 1-ml aliquot\* of the solution is transferred to a 15-ml test tube and thoroughly mixed with 2 ml of the buffered hydroxylamine solution. It is then mixed with 0.5 ml of the 1,10-phenanthroline solution. After 15 minutes the transmittance is measured in a spectrophotometer that has been adjusted with a blank at a wavelength of 490 nm. (A blank and suitable standard should be carried throughout the experiments. Reserve all used and unused solutions containing the rinsings from the broken fracture pieces.)

## ANALYSIS OF NICKEL

### Scope

The amount of nickel that is dissolved from a nickel steel (5.8% Ni) during the stress-corrosion cracking process is about 2 micrograms. Working at this nickel level,

\*If desired, the remaining 1-ml aliquot may be used to determine the ferrous iron present. To accomplish this, 2 ml of oxygen-free water is added instead of the buffered hydroxylamine solution. However, meaningful results are obtainable only if the entire experiment is conducted in an oxygen-free atmosphere.

it is necessary to combine and rework all used and unused iron solutions from a given specimen and to develop the nickel-dimethylglyoxime color complex in a final volume of 3 ml.

#### Apparatus

A spectrophotometer capable of providing transmittance data on as little as 3 ml of the nickel color complex was used.

#### Reagents

Ammoniacal Dimethylglyoxime Solution — Dimethylglyoxime (1 g) is dissolved in 100 ml of concentrated ammonium hydroxide.

Bromine Water — About 5 ml of bromine is mixed thoroughly with 100 ml of water and stored in a glass-stoppered bottle.

Citric Acid Solution (10%) — Citric acid (10 g) is dissolved in 75 ml of water and diluted to 100 ml.

Standard Nickel Stock Solution (1 ml = 20  $\mu$ g Ni) — High-purity nickel (20.0 mg) is dissolved in 5 ml of nitric acid, rinsed down with water, boiled to expel the oxides of nitrogen, cooled, diluted to the mark in a 1000 ml volumetric flask, and mixed thoroughly.

Standard Nickel Working Solution (1 ml = 2  $\mu$ g Ni) — A 10-ml aliquot of the standard nickel stock solution is transferred to a 100-ml volumetric flask, diluted to the mark with water, and mixed.

#### Procedure

All of the used and unused solutions, rinsings included, reserved from the iron determination are transferred to a 50-ml beaker, rinsing the containers successively with two 2-ml volumes of water. The solution is evaporated to dryness, then after the addition of 5 ml of nitric acid and 3 ml of perchloric acid it is evaporated to fumes and cooled. The cover is rinsed and the solution is again evaporated to dryness in an open beaker under a protective plastic shield to prevent contamination. After dissolving the salts with 3 ml of hydrochloric acid and rinsing the beaker with a little water, the solution, in an open beaker, is carefully evaporated to a volume of about 0.1 or 0.2 ml. Following the addition of 1 ml of water and a small piece of congo red paper, ammonium hydroxide is added until the paper just turns red. Immediately hydrochloric acid (1:3) is added from a dropping pipette until the paper just turns blue. The test paper is removed, and with thorough shaking in each instance, the following reagents are added in the order listed: 4 drops of citric acid solution, 6 drops of bromine water, 2 drops of ammoniacal dimethylglyoxime, and 2 drops of ammonium hydroxide. The solution is transferred to a small test tube that has been calibrated with a 3-ml mark, diluted to the mark, and mixed thoroughly. After transferring the solution to an absorption tube and letting it stand for 15 minutes, the transmittance is measured in a spectrophotometer that has been properly adjusted with a blank at a wavelength of 530 nm. (The blank and a suitable standard should be carried throughout the experiment.)

## ANALYSIS OF CHROMIUM

### Scope

The amount of chromium that is dissolved from a chromium steel (11.6% Cr) during stress-corrosion cracking is about 1.4 micrograms. As with nickel, it is necessary to combine and rework all used and unused iron solutions from a given sample and develop the chromium-diphenylcarbazide color complex in a final volume of 10 ml.

### Apparatus

A spectrophotometer capable of providing transmittance data on as little as 10 ml of the chromium color complex was used.

### Reagents

Ammonium Persulfate Solution (25%) -- Ammonium persulfate (25 g) is dissolved in 100 ml of water.

Diphenylcarbazide Solution -- Diphenylcarbazide (0.05 g) is dissolved in 10 ml of acetone and diluted with 10 ml of water. This solution is prepared fresh as needed.

Silver Nitrate Solution (0.5%) -- Silver nitrate (0.5 g) is dissolved in 100 ml of water.

Sodium Hydroxide Solution (5%) -- Sodium hydroxide (5 g) is dissolved in 100 ml of water.

Sodium Peroxide, 20 mesh and finer.

### Procedure

All of the used and unused solutions, rinsings included, reserved from the iron determination are transferred to a 150-ml beaker and evaporated without boiling to near dryness in an open beaker. After adding 5 ml of nitric acid and 1 ml of sulfuric acid the organic matter is destroyed by evaporating the solution to sulfur trioxide fumes. (If the solution appears brownish, the fuming process is repeated after a few drops of nitric acid is carefully added to the hot solution.) The solution is cooled, rinsed down, and diluted to about 35 ml with water. A small piece of congo red paper is inserted, then sodium hydroxide solution is added until the test paper just turns red. After removing the test paper, about 0.5 g of sodium peroxide is added and the solution is boiled for 10 minutes, then cooled, diluted to exactly 50 ml in a test tube, mixed, and allowed to stand overnight. Without disturbing the precipitated ferric hydroxide lying at the bottom of the test tube, 40 ml, two 20-ml aliquots withdrawn with a propipette, is transferred to a 150-ml beaker and made just acidic to congo red test paper with (1:1) sulfuric acid. The test paper is removed and three more drops of the same acid is added in excess. After adding 1 ml of the 0.5% silver nitrate and 2 ml of the 25% ammonium persulfate reagents, the solution is boiled for 30 minutes in a covered beaker. The volume is decreased to about 9 ml by evaporation in an open beaker, then cooled and adjusted to the mark in a 10-ml volumetric flask. After adding 0.5 ml of the diphenylcarbazide solution, mixing, transferring the solution to an absorption cell, and letting it stand for 5 minutes, the transmittance is measured in a spectrophotometer that has been adjusted with a blank solution at a wavelength of 525 nm. (The blank and a suitable standard should be carried throughout the experiment.)

## ANALYSIS OF MOLYBDENUM

### Scope

The amount of molybdenum that is dissolved from a molybdenum steel (1.9% Mo) during stress-corrosion cracking is about  $0.25 \mu\text{g}$  per sample specimen, making it necessary to combine all of the used and unused iron solutions from two specimens to obtain a measurable amount of the molybdenum thiocyanate color complex.

### Apparatus

A spectrophotometer capable of providing transmittance data on 3 ml of the butyl acetate extract of the molybdenum thiocyanate color complex was used.

### Reagents

#### Butyl Acetate, Reagent Grade

Sodium Thiocyanate Solution (5%) -- Sodium thiocyanate (50 g) is dissolved in 1000 ml of water.

Stannous Chloride Solution -- Stannous chloride dihydrate (112 g) is dissolved in 130 ml of hydrochloric acid and diluted to 1000 ml with water.

### Procedure

All of the used and unused solutions, rinsings included, reserved from the iron determination on two specimens are transferred to a 150-ml beaker, evaporated to dryness, and baked to destroy most of the salts. Upon cooling, 5 ml of nitric acid and 2 ml of perchloric acid are added. With the beaker covered, the solution is evaporated until perchloric acid refluxes quietly from the cover glass. After cooling, the beaker is rinsed down with about 10 ml of water; its contents is boiled 1 minute to expel chlorine and again cooled. The solution is then transferred to a 125-ml separatory funnel and shaken vigorously for 10 seconds with 10 ml of the sodium thiocyanate solution, then for 10 seconds with 10 ml of the stannous chloride solution. After adding exactly 50 ml of butyl acetate, the solution is shaken vigorously for 20 seconds and allowed to stand until the layers separate completely. The aqueous layer is withdrawn and the butyl acetate layer shaken for 10 seconds after each addition of two 10-ml portions of diluted (1:1) stannous chloride solutions; following each shaking period, sufficient time is allowed for the layers to separate completely before the aqueous layer is withdrawn and discarded. The butyl acetate layer is filtered through a dry 9-cm No. 40 Whatman filter paper, the filtrate being caught in a clean dry absorption tube. The transmittance is immediately measured in a spectrophotometer that has been adjusted with reagent-grade butyl acetate at a wavelength of 475 nm. (A blank and suitable standard should be carried throughout the experiment.)

## ANALYSIS OF MANGANESE

### Scope

As the amount of manganese dissolved from a manganese steel (5.5% Mn) during the stress-corrosion cracking process is about  $2 \mu\text{g}$  per specimen, it is necessary to combine all of the used and unused iron solutions from two specimens to obtain a measurable amount of the colored permanganic acid ion.

### Apparatus

A spectrophotometer capable of providing transmittance data on a 4-ml solution of the manganese, as permanganic acid, rinsed from two sample specimens was used.

### Reagent

Potassium Periodate Solution — Potassium periodate (20 g) is dissolved in 750 ml of water and diluted with 250 ml of phosphoric acid.

### Procedure

All of the used and unused solutions, rinsings included, reserved from the iron determination on two specimens are transferred to a 150-ml beaker, evaporated to dryness, and baked in a furnace at 300°C for 15 minutes to expel the volatile salts. After cooling and adding 5 ml of nitric acid and 3 ml of perchloric acid, the beaker is covered and the contents evaporated until perchloric acid refluxes quietly from the beaker cover. The beaker is cooled and rinsed down with water. With the cover removed, the solution is evaporated to a volume of about 0.1 ml, cooled, then boiled vigorously with 10 ml of water until the volume is about 4 ml. After rinsing the beaker with a little water and adding 1 ml of the potassium periodate solution, the contents are boiled gently for 10 minutes or until the total volume is slightly less than 4 ml. The beaker is cooled and the contents transferred to an absorption tube that has been previously calibrated with a 4-ml mark. The volume is adjusted exactly to 4 ml with water that has been freshly boiled and cooled. The sample is mixed and its transmittance measured in a spectrophotometer that has been adjusted with water at a wavelength of 525 nm. (A blank and suitable standard should be carried throughout the entire experiment.)

### DISCUSSION

In the initial quantitative tests, considerable emphasis was placed on determining the amount of ferrous ions generated within the stress-corrosion cracks. To obtain the highest and most meaningful value for the ferrous ion content, it is necessary to conduct the experiments with the least amount of manipulation possible and in a nearly oxygen-free medium. By working in an atmosphere of carbon dioxide and using freshly boiled and cooled distilled water to rinse the specimens, it was established that approximately 80% of the iron was in the ferrous state.

As the experiments progressed, less emphasis was placed on the ferrous ion content, but the manipulative details were retained.

It was found that each sample section was effectively rinsed with the dropwise addition of 1.8 ml of oxygen-free distilled water, each drop being directed to fall on that area of the sample section where the crack was initiated, then flowing along the length of the crack surface before being collected. Rerinsing the specimen sections showed no measurable amounts of iron to be present.

Table I shows typical amounts of iron and alloying constituents rinsed from stress-corrosion crack surfaces of a carbon steel and of steels containing nickel, chromium, molybdenum, and manganese, respectively.

Table 1  
Typical Analysis of Rinsings from Stress-Corrosion  
Crack Surfaces of Various Types of Research Steels

Material	Elements Found in the Leach Solution (μg per sample)					Percent of Alloying Element Present	
	Fe	Ni	Cr	Mo	Mn	in Material	in Rinse
Carbon Steel	20.8	—	—	—	—	0.45 C	Not determined
Nickel Steel	21.5	1.7	—	—	—	5.8 Ni	7.3 Ni
Chromium Steel	12.8	—	1.4	—	—	11.6 Cr	9.9 Cr
Molybdenum Steel	15.6	—	—	0.25	—	1.9 Mo	1.6 Mo
Manganese Steel	13.8	—	—	—	1.8	5.5 Mn	11. Mn

The analyses of the rinsings of the nickel, chromium, and molybdenum steels reflect roughly their alloy content. Analysis of the rinsings of the manganese steel shows a much greater manganese content in solution than exists in the alloy. Figure 1, a photo-micrograph of a cracked manganese steel specimen, shows the crack to follow largely the dark streaks of the specimen. Examination of these areas with the scanning-electron microprobe reveals the darkish areas to contain over 1.5 times as much manganese as the light areas. This largely accounts for the relatively high manganese content of the rinse solution.



Fig. 1 - Manganese steel (magnification 200X)

**SUMMARY**

The foregoing spectrophotometric procedures provide a means for determining the amounts of iron, and alloying constituents that may undergo dissolution in stress-corrosion cracks in carbon steels and in nickel, chromium, molybdenum, and manganese steels. To measure the small amounts of iron ions and still smaller amounts of alloying constituent ions, each procedure provides for the transmittance measurements to be made at a low final volume (usually 3 ml) to increase sensitivity.

Excepting the carbon steel, the analysis of any given binary alloy specimen involved the determination of iron and the accompanying alloying constituent that was dissolved during the stress-corrosion cracking process; the iron was determined first, then all of the iron solutions, used and unused, were combined and reworked to determine the pertinent alloying constituent. Under the conditions of the experiment, the determination of nickel and chromium in their respective alloys required the combined rinsings from one specimen only. The combined rinsings from two specimens were required for the determination of molybdenum and manganese.

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1. Brown, B.F., Fujii, C.T., and Dahlberg, E.P., *J. Electrochemical Soc.* 116:218 (1969)
2. Sandoz, G., Fujii, C.T., and Brown, B.F., "Solution Chemistry Within Stress-Corrosion Cracks in Alloys," to be published in *Corrosion Science*

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Working at final volume levels as low as 3 ml, spectrophotometric procedures have been developed for the determination of very small amounts of ferrous, ferric, and alloying-constituent ions formed within stress-corrosion cracks in carbon steels and in steels containing nickel, chromium, molybdenum, and manganese, respectively.	

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1. Page 1, 5th par., 2nd line should read "fracture surfaces of a given specimen . . . "
2. Page 5, "Procedure," 9th line. Change 50 ml to 5 ml.

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